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Swelling behaviours of *N*-alkylacrylamide gels in water: effects of copolymerization and crosslinking density

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N-isopropylacrylamide (NIPA)/*N*-n-propylacrylamide (NNPA) copolymer gels of various molar ratios were prepared by radical polymerization and the relationship between the swelling behaviour of the gels and the copolymerization ratio was studied experimentally. The effect of a crosslinking point on the swelling behaviour of the NIPA gels was investigated by preparing the gels with various crosslinking densities. The results of our experiments revealed that the transition temperatures of the NIPA/NNPA copolymer gels were changed in proportion to the monomer ratio used in copolymerization and that the crosslinking density strongly affected the swelling ratios but not the transition temperatures of the gels.

(Keywords: *N*-alkylacrylamide gels; swelling behaviour; crosslinking density)

INTRODUCTION

It is well known that the phase transitions of gels are induced by a continuous change in various conditions of the surroundings, such as the ionic concentration of the network, temperature, pH, solvent composition, etc.[1–3]. Thermodynamically, the swelling equilibrium of gels can be deduced from the free energy of these materials which results from the elasticity, the free energy of mixing and the osmotic pressure of the counterions[4].

It has been reported that varying the temperature can cause *N*-alkylacrylamide gels to undergo volume phase transition in water[5]. Since *N*-alkylacrylamide gels are non-ionic, their swelling equilibrium is governed by the elasticity of the gel and by the free energy of mixing that results from the interaction between the polymer network and water molecules[6]. Hydrophobic interaction has been shown to play an important role in the phase transition of the *N*-alkylacrylamide gel in water[6,7]. Therefore, it is expected that the change in hydrophobicity of the gel network or property of the solvent being used brings about the change in the swelling behaviour of the gels.

There have been many reports of attempts to control the thermally induced volume phase transition of *N*-alkylacrylamide gels, for example through the use of mixed solvents[7,8], the addition of salt[9], the copolymerization of an electrolyte monomer[10], and the addition of surfactants[11–13]. A previous paper of ours showed that the swelling behaviour of three *N*-alkylacrylamide gels, namely *N*-n-propylacrylamide (NNPA), *N*-isopropylacrylamide (NIPA) and *N*-cyclopropylacrylamide (NCPA), was strongly dependent on the hydrophobicity of the specific *N*-alkyl group[5]. The transition temperature of the NNPA gel was $\sim$24°C, which was 10 K lower than that of the NIPA gel (34°C), while the NCPA gel, which is relatively less hydrophobic than both the NIPA and NNPA gels, showed continuous swelling–deswelling behaviour without undergoing a volume phase transition. The swelling ratios of the gels were remarkably similar in both the completely collapsed and expanded regions. This suggests that the hydrophobicity of the *N*-alkyl group in the side chain significantly affects the transition temperature of the thermally induced phase transition, whereas the swelling ratio in the swollen state may be mainly influenced by the elastic contribution or the nature of the network backbone.

In this work, in an attempt to investigate the above points, various NIPA/NNPA copolymer gels, and NIPA gels of various crosslinking densities were synthesized and their swelling behaviours in water were examined.

EXPERIMENTAL

Materials

The NIPA monomer, provided by Eastman Kodak, was purified by recrystallization from a benzene/n-hexane mixture. The NNPA monomer was synthesized according to the method reported by Itoh[14], and purified by vacuum distillation under a nitrogen atmosphere. The initiator used in this study was potassium persulfate (KPS), which was recrystallized from water. *N*, *N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), a special grade reagent supplied by Tokyo Kasei, was used as an accelerator without further purification. *N*,*N'*-methylenebisacrylamide (BIS) (special grade reagent), supplied by Tokyo Kasei, was used as a crosslinking agent, without further purification.

Sample preparation

NIPA/NNPA copolymer gels (monomer ratios, 0:100, 25:75, 50:50, 75:25 and 100:0; total concentration of the monomers, 700 mM) were prepared by radical

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polymerization (initiator, KPS; accelerator, TMEDA; crosslinking agent, BIS (7 mM)) in water at 0°C. To investigate the effect of the crosslinking density, NIPA (700 mM) gels with different BIS contents (1.75, 3.5, 7, 14, and 28 mM) were prepared by radical polymerization (initiator, KPS; accelerator, TMEDA) in water at 0°C.

Procedures

The volumes of the gels were measured by calibrated-scale photography, as follows. As a reference volume, we adopted the volume, V_0, where the gel was synthesized in a capillary glass tube with a diameter, d_0, of 1.6 mm. After equilibration, the diameter of the gel, d, was measured for each condition by calibrated scale photography. The swelling ratio of the gel, V/V_0, was calculated from d and d_0 by using the relationship $V/V_0=(d/d_0)^3$.

The transition temperatures of the gels were measured by thermal analysis using a differential scanning calorimeter (Seiko I. Inc., Model SSC-5000 DSC-100). The thermal analysis procedure was described in a previous paper from this laboratory[7].

RESULTS

Figure 1 shows the swelling curves of the NIPA gel, NNPA gel and the NNPA/NIPA copolymer gels (molar ratios, 25/75, 50/50, and 75/25). It can be clearly seen that the transition temperature increases linearly with the molar ratio of NNPA/NIPA, while the swelling in both the swollen and shrunken states is almost the same for all of the gels. The transition temperatures, determined by d.s.c., are plotted against the NIPA content (mol%) of the gels in *Figure 2*. The points for 0 and 100 mol% of NIPA indicate the transition temperatures of the NNPA and NIPA homopolymer gels, respectively. The transition temperatures of the NNPA/NIPA copolymer gels were proportional to the mole percentage of the NIPA (0, 25, 50, 75, and 100). These results are consistent with the results obtained in previous work with other copolymer gels[1,5], and indicated that the transition temperatures of the alkylacrylamide gels could be controlled by copolymerization within the range of the transition temperatures of the homopolymer gels.

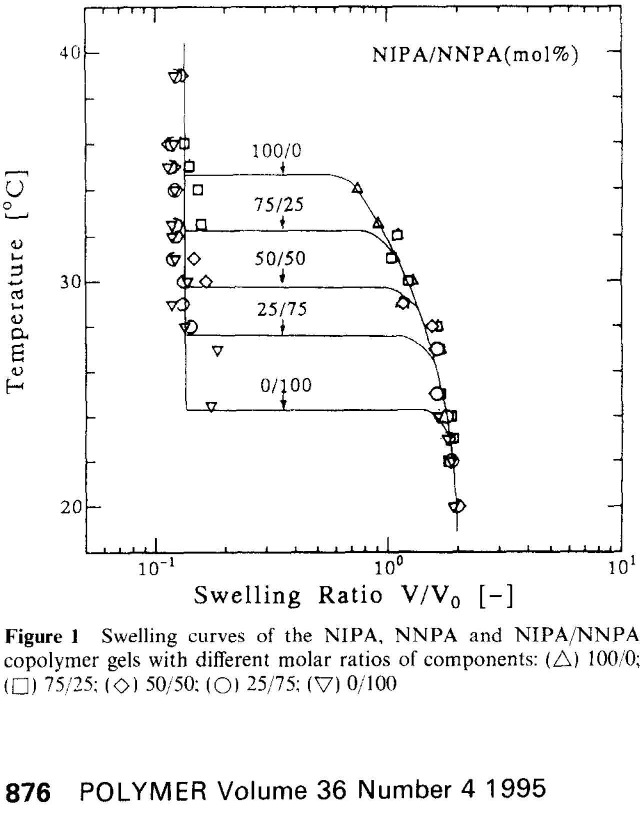

Figure 1 Swelling curves of the NIPA, NNPA and NIPA/NNPA copolymer gels with different molar ratios of components: (△) 100/0; (□) 75/25; (◇) 50/50; (○) 25/75; (▽) 0/100

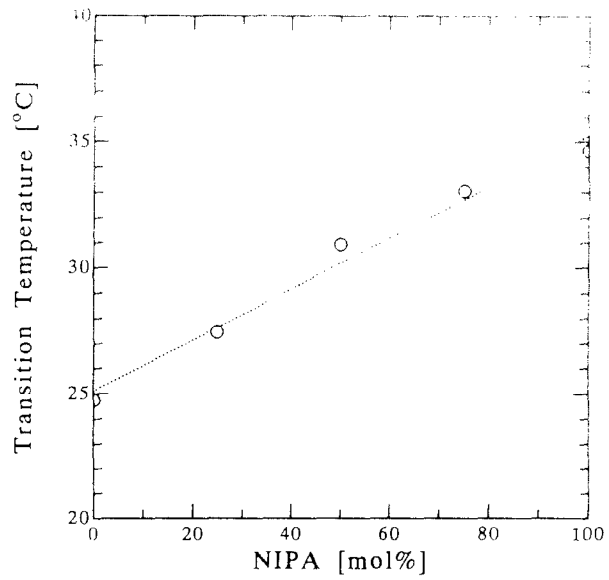

Figure 2 Transition temperatures of the NIPA/NNPA copolymer gels as a function of NIPA content

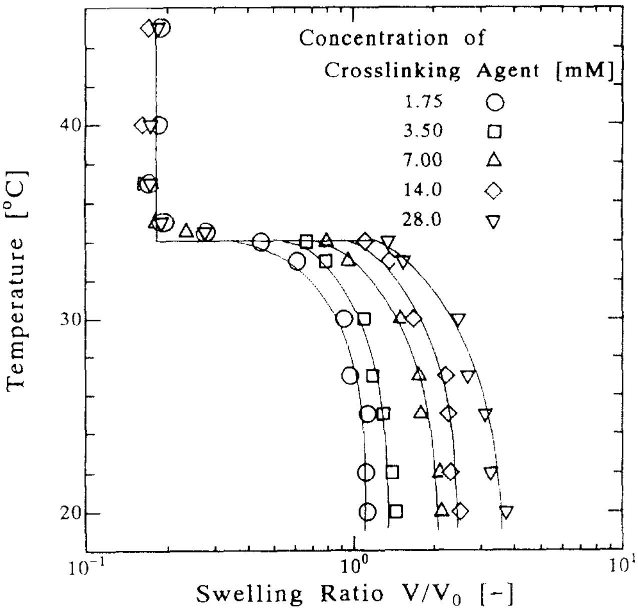

Figure 3 Swelling curves of the NIPA gels prepared at various BIS concentrations

It was also found that the copolymerization of NIPA and NNPA did not significantly affect the swelling ratio in the completely expanded and collapsed regions. Compositional changes in the various copolymers seemed to result in changes in the gels' osmotic pressures, owing to interactions between the polymer segments and water (the mixing term in the theory of Tanaka *et al.*[4]). Therefore, the results indicated that the contribution of the mixing term of the gels' osmotic pressures may not control the swelling in the expanded and collapsed states,

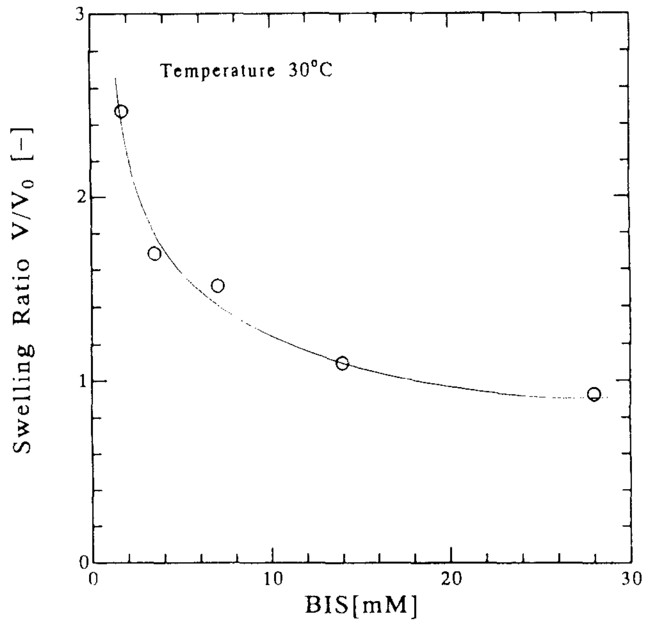

Figure 4 Plots of the swelling ratios of the NIPA gels, measured at 30°C, as a function of BIS concentration

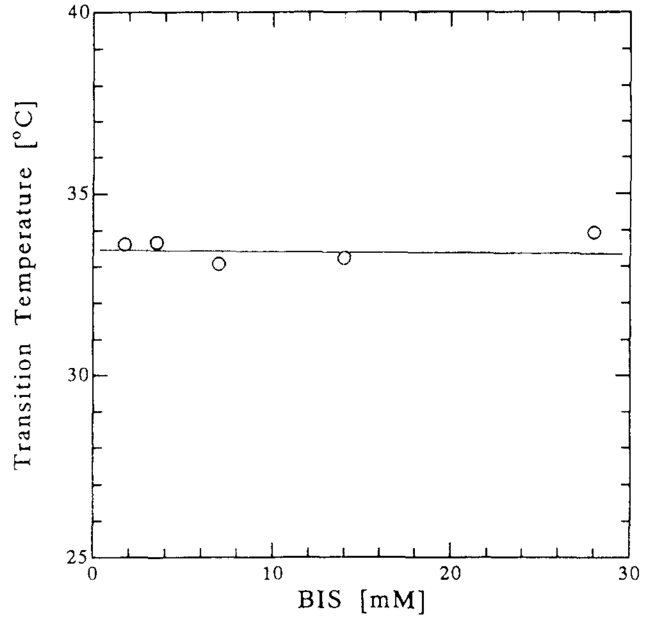

Figure 5 Plots of the transition temperatures of the NIPA gels as a function of BIS concentration

but does so in the transition region. In other words, the elastic contribution of the gels' osmotic pressures may be dominant in the expanded state.

We then examined the effect of the crosslinking point on the swelling equilibria. It is expected from the previous work by Hirokawa *et al.*[15] that the swelling ratio of a gel decreases as the crosslinking density of the gel increases. *Figure 3* shows the swelling curves of the NIPA gels prepared using various concentrations of the crosslinking agent BIS (1.75, 3.5, 7, 14, and 28 mM). As expected, the concentration of the BIS mainly affected the swelling ratios of the NIPA gels in the swollen region, but had only slight effects on the swelling ratios in the collapsed region and the transition temperatures. *Figure 4* shows plots of the swelling ratio in the swollen state (at 30°C) against the BIS concentration; it can be seen that there was a tendency for the swelling ratios to decrease as the BIS concentration increased. The transition temperatures of the gels were carefully determined by d.s.c. and are plotted against the BIS concentration in *Figure 5*. The transition temperatures of the gels were independent of the BIS concentration.

CONCLUSIONS

This paper has shown experimentally that the transition temperatures of various *N*-alkylacrylamide gels in water could be changed by varying the amounts of the two thermosensitive components in a copolymerization reaction, and also that the swelling ratio of the gels in the swollen region could be adjusted by altering the content of the crosslinking reagent.

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